

[54] **PHOTOPOLYMERIZABLE COMPOSITIONS CONTAINING A KETO DIOXOLANE AS THE PHOTSENSITIZER**

[75] Inventor: **William R. Adams, Oakland, N.J.**

[73] Assignee: **Sun Chemical Corporation, New York, N.Y.**

[21] Appl. No.: **628,836**

[22] Filed: **Nov. 4, 1975**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 368,677, June 11, 1973, Pat. No. 3,944,509.

[51] Int. Cl.² **C08F 2/46; C08F 4/00**

[52] U.S. Cl. **428/522; 96/115 P; 260/340.9; 204/159.23; 427/44; 427/54; 428/35; 428/441; 428/451; 428/454; 428/461; 428/515**

[58] Field of Search **260/340.9; 204/159.23, 204/159.24; 96/115 P**

[56] **References Cited**

U.S. PATENT DOCUMENTS

3,607,693 9/1971 Heine et al. 204/159.15

Primary Examiner—Richard B. Turer
Attorney, Agent, or Firm—Cynthia Berlow

[57] **ABSTRACT**

Ethylenically unsaturated monomeric esters in the presence of keto-dioxolane compounds are photocured upon exposure to a source of radiation.

8 Claims, No Drawings

PHOTOPOLYMERIZABLE COMPOSITIONS CONTAINING A KETO DIOXOLANE AS THE PHOTOSENSITIZER

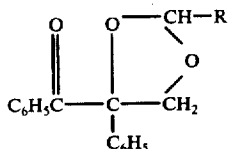
This application is a continuation-in-part of applica- 5
tion Ser. No. 368,677, filed June 11, 1973 now U.S. Pat.
No. 3,944,509, issued Mar. 16, 1976.

This invention relates to the use of keto-dioxolane 10
compounds as photoinitiators for ethylenically unsatu-
rated monomeric esters.

The use of photopolymerizable ethylenically unsatu-
rated monomeric materials in coating compositions,
printing inks, adhesives, and the like is known. It is also
known that such monomeric materials are converted 15
into polymers by the action of radiation and that they
will polymerize at an improved rate when exposed to
radiation in the presence of a photoinitiator.

It has now been found that polymers of ethylenically
unsaturated monomeric esters having improved curing
speeds can be obtained with no sacrifice of quality of 20
the product by carrying out the photopolymerization in
the presence of a novel keto-dioxolane compound.

The sensitizers of this invention have the following
structure:



wherein R is alkyl of up to about nine carbon atoms,
e.g., pentyl, octyl, or 2-ethylhexyl; alkyl of from one to
about nine carbon atoms substituted with at least one 35
halogen (chlorine, bromine, iodine, or fluorine), alkoxy,
or the like; phenyl; phenyl substituted with at least one
halogen, alkoxy, hydroxy, nitro, carboalkoxy, alkylami-
ne, carboxyalkenyl wherein the alkenyl group has
about two to six carbon atoms, or the like; heterocyclic 40
group of about three to twelve ring-carbon atoms; or
cycloalkyl of five to eight ring-carbon atoms.

Examples of these derivatives include, but are not
limited to, 2-trichloromethyl-4-benzoyl-4-phenyl-1, 3-
dioxolane; 2-(p-dimethylaminophenyl)-4-benzoyl-4- 45
phenyl-1, 3-dioxolane; 2-cinnamyl-4-benzoyl-4-phenyl-
1, 3-dioxolane; 2-furyl-4-benzoyl-4-phenyl-1, 3-dioxo-
lane; and the like; and mixtures thereof.

The acyloin derivatives of this invention may be pre- 50
pared by any known and convenient means, such as for
example by the acid-catalyzed condensation of alpha-
methylolbenzoin with an aliphatic or an aromatic alde-
hyde, e.g., p-dimethylaminobenzaldehyde, acetalde-
hyde, chloral, furfural, and the like.

These keto-dioxolane derivatives are effective initia- 55
tors in the photopolymerization of a broad range of
polymerizable ethylenically unsaturated monomeric
compounds. Such a compound is generally a monomer
or prepolymer, that is, a dimer, trimer, or other oligo-
mer or mixture or copolymer thereof, generally de- 60
scribed as the acrylic acid, methacrylic acid, itaconic
acid, and the like, ester of an aliphatic polyhydric alco-
hol such as for example the di- and polyacrylates, the di-
and polymethacrylates, and the di- and polyitaconates
of ethylene glycol, triethylene glycol, tetraethylene 65
glycol, tetramethylene glycol, trimethylolethane, tri-
methylolpropane, butanediol, pentaerythritol, dipenta-
erythritol, tripentaerythritol, other polypentaery-

thritols, sorbitol, d-mannitol, diols of unsaturated fatty
acids, and the like.

Typical compounds include, but are not limited to,
trimethylolpropane triacrylate, trimethylolethane tri-
acrylate, trimethylolpropane trimethacrylate, trimeth-
ylolethane trimethacrylate, tetramethylene glycol di-
methacrylate, ethylene glycol dimethacrylate, triethyl-
ene glycol dimethacrylate, tetraethylene glycol diacry-
late, pentaerythritol diacrylate, pentaerythritol triacryl-
ate, pentaerythritol tetraacrylate, dipentaerythritol di-
acrylate, dipentaerythritol triacrylate, dipentaerythritol
tetraacrylate, dipentaerythritol pentaacrylate, dipenta-
erythritol hexacrylate, tripentaerythritol octoacrylate,
pentaerythritol dimethacrylate, pentaerythritol trimeth-
acrylate, dipentaerythritol dimethacrylate, dipentaery-
thritol tetramethacrylate, tripentaerythritol octametha-
crylate, pentaerythritol diitaconate, dipentaerythritol
transitaconate, dipentaerythritol pentaitaconate, dipen-
taerythritol hexaitaconate, ethylene glycol dimethacry-
late, 1,3-butanediol diacrylate, 1,3-butanediol dimethacry-
late, 1,4-butanediol diitaconate, sorbitol triacrylate,
sorbitol tetraacrylate, sorbitol tetramethacrylate, sorbi-
tol pentaacrylate, sorbitol hexacrylate, and the like, and
modifications, mixtures, and prepolymers thereof.

Although the ratio of the amount of ester to the
amount of photoinitiator may be about 10-99:1-90, it is
generally about 90-99:1-10.

Commonly known modifiers may be incorporated
into the formulations using these compositions, includ-
ing plasticizers; wetting agents for the colorant, such as
dichloromethylstearate and other chlorinated fatty est-
ers; leveling agents, such as lanolin, paraffin waxes, and
natural waxes; and the like. Such modifiers are gener-
ally used in amounts ranging up to about 3 percent by
weight, preferably about 1 percent, based on the total
weight of the formulation.

The formulations may be prepared in any known and
convenient manner. Variables which determine the rate
at which a photopolymerizable composition will dry
include the nature of the substrate, the specific ingredi-
ents in the composition, the concentration of the photo-
initiator, the thickness of the material, the nature and
intensity of the radiation source and its distance from
the material, the presence or absence of oxygen, and the
temperature of the surrounding atmosphere. Irradiation
may be accomplished by any one or a combination of a
variety of methods. The composition may be exposed,
for example, to actinic light from any source and of any
type as long as it furnishes an effective amount of ultra-
violet radiation, since the compositions activatable by
actinic light generally exhibit their maximum sensitivity
in the range of about 2000A. to 7000A., and preferably
about 2000A. to 4000A.; gamma radiation emitters; and
the like; and combinations of these. Suitable sources
include, but are not limited to, carbon arcs, mercury
vapor arcs, pulsed xenon lamps, fluorescent lamps with
special ultraviolet light-emitting phosphors, argon glow
lamps, photographic flood lamps, and so forth.

The time of irradiation must be sufficient to give the
effective threshold dosage. Irradiation may be carried
out at any convenient temperature, and most suitably is
carried out at room temperature for practical reasons.
Distances of the radiation source from the work may
range from about 1 inch to 6 feet, and preferably about
5 inches to 4 feet.

When cured by radiation, the compositions are dry,
flexible, abrasion resistant, and chemical resistant; also

they have excellent ink receptivity, hydrophilic-hydrophobic balance, dot resolution, and initial roll-up, making them particularly suitable in such applications as presensitized lithographic printing plates and photore-sists. The compositions are also useful as binders for magnetic tape; printing inks; adhesives for foils, films, papers, fabrics, and the like; coatings for metals, plas-tics, paper, wood, foils, textiles, glass cardboard, box board, and the like; markers for roads, parking lots, airfields, and similar surfaces, and so forth. Stock which may be printed includes paper, clay-coated paper, and box board. In addition, the compositions are suitable for the treatment of textiles, both natural and synthetic, e.g., in vehicles for textile printing inks or for special-ized treatments of fabrics to produce water repellency, oil and stain resistance, crease resistance, etc.

When used as vehicles for inks, e.g., printing inks, the compositions may be pigmented with any of a variety of conventional organic or inorganic pigments, e.g., molybdate orange, titanium dioxide, lithol rubine red, di-arylide yellow, chrome yellow, phthalocyanine blue, zinc oxide, and carbon black, as well as colored with dyes in a conventional amount. The vehicle may be used in an amount ranging from about 20 to 99.9 percent and the amount of colorant may range from about 0.1 to 80 percent of the weight of the total composition.

Typical laminations using the compositions of this invention as adhesives include polymer-coated cellophane to polypropylene, Mylar to a metal such as alumi-num or copper, polypropylene to aluminum, and the like.

The compositions may also be utilized for metal coat-ings and particularly for metals which are to be subse-quently printed. Glass and plastics may also be printed or coated, and the coatings are conventionally applied by roller or spray. Pigmented coating systems may be used for various polyester and vinyl films; glass; poly-mer-coated cellophane; treated and untreated polyethy-lene, for example in the form of disposable cups or bottles; treated and untreated polypropylene; and the like. Examples of metals which may be coated include sized and unsized tin plate.

Photopolymerizable elements prepared from these compositions comprise a support, e.g., a sheet or plate, having superimposed thereon a layer of the above-described photopolymerizable materials. Suitable base or support materials include metals, e.g., steel, alumi-num, or copper, plates; sheets; and foils; and films or plates composed of various film-forming synthetic resins or high polymers. Fillers or reinforcing agents can be present in the synthetic resin or polymer bases. In addition, highly reflective bases may be treated to ab-sorb ultraviolet light, or a light absorbtive layer can be transposed between the base and photopolymerizable layer.

Photopolymerizable elements can be made by expos-ing to radiation selected portions of the photopolymer-izable layer thereof until addition polymerization is completed to the desired depth in the exposed portions. The unexposed portions of the layer are then removed, e.g., by the use of solvents which dissolve the monomer or prepolymer but not the polymer.

When used as printing inks, coating compositions, and adhesives, the compositions described herein are used without volatile solvents and possess many advantages over conventional oleoresinous and solvent-type inks and coatings. The substrate need not be pretreated or prepared in any way. The use of volatile solvents and

the attendant health and fire hazards and odor are elimi-nated. The inks and coatings have excellent adhesion to the substrate after exposure to radiation. They have good gloss and rubresistance and withstand tempera-tures as high as about 150° C. and as low as about -20° C. The printed or coated sheets can be worked and further processed immediately after exposure to the energy source.

The invention and its advantages will be better under-stood with reference to the following illustrative exam-ples, but it is not intended to be limited thereto. In the samples, the parts are given by weight unless otherwise specified. Unless otherwise indicated, when an ingredi-ent is solid at room temperature, the mixture may be heated to melt the solid ingredient, but generally not above 100° C., or it may be used in a mixture with other liquid ingredients. The atmospheric and temperature conditions were ambient unless otherwise noted.

EXAMPLE 1

A mixture of 24.2 grams (0.1 mole) of α -methylolben-zoin, 14.9 grams (0.1 mole) of *p*-dimethylaminoben-zaldehyde, and 1.0 grams of *p*-toluenesulfonic acid was dissolved into 125 ml. of toluene and placed into a Dean-Stark apparatus. The reaction mixture was re-fluxed for 8 hours, and the theoretical amount of water was collected.

The solution was cooled, washed with 5% sodium carbonate solution, separated, and dried. Concentration under reduced pressure gave 32.3 grams of product melting at 118°-120° C.

Recrystallization from ethanol gave 29.6 grams (79.5% yield) of 2-(*p*-dimethylaminophenyl)-4-benzoyl-4-phenyl-1,3-dioxolane (m.p. 128°-129° C.). The ele-mental analysis was as follows:

	C	H	N
Calculated:	77.19	6.21	3.75
Found:	77.31	6.15	3.73

EXAMPLE 2

The procedure of Example 1 was repeated except that the starting materials were α -methylolbenzoin and chloral. The product was a 63% yield of 2-trichloromethyl-4-benzoyl-4-phenyl-1, 3-dioxolane, analyzed as follows:

	C	H	C ₁
Calculated:	54.91	3.50	28.67
Found:	55.03	3.49	28.50

EXAMPLE 3

The procedure of Example 1 was repeated except that the starting materials were α -methylolbenzoin and cin-namaldehyde. The product, 2-cinnamyl-4-benzoyl-4-phenyl-1, 3-dioxolane, was obtained in a yield of 73% and analyzed as follows:

	C	H
Calculated:	80.88	5.66
Found:	80.97	5.62

EXAMPLE 4

The procedure of Example 1 was repeated except that the starting materials were α -methylbenzoin and furfural. The product, 2-furyl-4-benzoyl-4-phenyl-1, 3-dioxolane, was obtained in a yield of 78% and analyzed as follows:

	C	H
Calculated:	74.99	5.03
Found:	74.56	5.07

EXAMPLE 5

A composition comprising 95 parts of isocyanate-modified pentaerythritol triacrylate and 5 parts of 2-(*p*-dimethylaminophenyl)-4-phenyl-1, 3-dioxolane was coated onto a glass slide at a wet-film thickness of 0.3 mil and irradiated at a distance of 1.5 inches from a 100-watt/inch ultraviolet lamp. The coating dried to a flexible abrasion-resistant film in 1.5 seconds.

EXAMPLE 6

A. The procedure of Example 5 was repeated with each of the following sensitizers instead of 2-(*p*-dimethylaminophenyl)-4-benzoyl-4-phenyl-1, 3-dioxolane:

TABLE I

Sensitizer	Cure speed, seconds
none	10.0
2-trichloromethyl-4-benzoyl-4-phenyl	3.0
2-cinnamyl-4-benzoyl-4-phenyl-1, 3-dioxolane	2.0
2-furyl-4-benzoyl-4-phenyl-1, 3-dioxolane	2.0

B. For comparative purposes, sensitizers outside of the scope of this invention were tested in the same manner as above with the following results:

TABLE II

	Cure time, seconds
Benzoin	15
α -methylbenzoin	6.0
α -phenylbenzoin	5.5
α -benzylbenzoin	7.5
benzoin acetate	11.5
α -methylbenzoin ethyl ether	12
benzil	11
benzophenone	25

Thus it can be seen that compositions containing the specific keto-dioxolane compounds of this invention (part A) cure considerably faster than comparable compositions containing related sensitizers that are not within the scope of this invention (part B).

EXAMPLE 7

The procedure of Example 5 was repeated with each of the following esters instead of isocyanate-modified pentaerythritol triacrylate. The results are tabulated below:

TABLE III

Ester	Cure speed, seconds
pentaerythritol tetraacrylate	2.1
triethanolpropane trimethacrylate	3.6
ethylene glycol dimethacrylate	7.0
triethylene glycol diacrylate	3.8
1,3-butanediol diacrylate	5.0
1,4-butanediol diitaconate	7.1
sorbitol pentaacrylate	4.3

EXAMPLE 8

A printing ink was prepared from the following:

	Parts by Weight
Product of Example 5	90
Phthalocyanine green	10

A glass bottle printed with this green ink was exposed to a 100-watt/inch ultraviolet lamp at a distance of 2 inches. The ink dried in 3.0 seconds. It had excellent adhesion to the glass and good grease- and rub-resistance.

EXAMPLE 9

The procedure of Example 8 was repeated with each of the following substrates instead of glass: clay-coated sulfite board, 32-pound coated paper, aluminum, and tin-free steel. The results were comparable.

EXAMPLE 10

A laminate was made of a film of polymer-coated cellophane and a film of oriented polypropylene with a mixture of the following ingredients between the two: 95 parts of trimethylolethane dimethacrylate and 5 parts of 2-trichloromethyl-4-benzoyl-4-phenyl-1, 3-dioxolane.

The laminate was exposed at a distance of 2.0 inches from a 100-watt/inch ultraviolet lamp. A tight bond was effected in 4.0 seconds.

EXAMPLE 11

The procedure of Example 10 was repeated with each of the following substrates: Saran-coated cellophane and Saran-coated cellophane, corona-discharge surface-treated polyethylene and coated cellophane, and polyvinylidene dichloride-coated polypropylene and Mylar.

The laminations were successful as evidenced by tear seals having bond strengths of at least 300 grams per inch.

EXAMPLE 12

The procedure of Examples 5-11 were repeated except that instead of being exposed to ultraviolet light the samples were passed on a conveyor belt beneath the beam of a Dynacote 300,000-volt linear electron accelerator at a speed and beam current so regulated as to produce a dose rate of 0.5 megarad.

These systems produced resinous materials of varying degrees of hardness in films from 0.5 to 20 mils thick having tacky surfaces.

EXAMPLE 13

The procedure of Examples 5-11 were repeated except that instead of being exposed to ultraviolet light the samples were exposed to a combination of ultraviolet light and electron beam radiation in a variety of arrangements: ultraviolet light, then electron beam; electron beam, then ultraviolet light; ultraviolet light before and after electron beam; electron beam before and after ultraviolet radiation; and simultaneous electron beam and ultraviolet light radiation. The results were comparable.

What is claimed is:

1. A photopolymerizable composition consisting essentially of about 10-99 parts of (a) an ethylenically unsaturated monomeric ester and about 1-90 parts of (b)

7

8

a photosensitizer selected from the group consisting of 2-trichloromethyl-4-benzoyl-4-phenyl-1, 3-dioxolane, 2-(p-dimethylaminophenyl)-4-benzoyl-4-phenyl-1,3-dioxolane, 2-cinnamyl-4-benzoyl-4-phenyl-1,3-dioxolane, and 2-furyl-4-benzoyl-4-phenyl-1,3-dioxolane.

2. The composition of claim 1 wherein the ratio of the amount of ester (a) to sensitizer (b) is about 90-99:1-10.

3. A photopolymerizable printing ink comprising the composition of claim 1 and a colorant.

4. A photopolymerizable coating composition comprising the composition of claim 1.

5. A photopolymerizable adhesive comprising the composition of claim 1.

6. A photopolymerizable element comprising a support and a coating thereon of the composition of claim 1.

7. A method of producing polymeric material which comprises exposing to a source of radiation about 10-99 parts of an ethylenically unsaturated monomeric ester in the presence of about 1-90 parts of the photosensitizer of claim 1.

8. The method of claim 7 wherein the photosensitizer is employed in an amount within the range of about 1-10 percent, based on the total weight of the composition.

* * * * *

15

20

25

30

35

40

45

50

55

60

65